

## RAPID THERMAL DECOMPOSITION OF BITUMINOUS COALS

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## INTRODUCTION

Pyrolysis studies of coals and chars have been pursued mainly with the objective of gaining knowledge about the kinetics of reaction processes involved in combustion and gasification. Slow heating studies are numerous,<sup>1/</sup> but they have little relevance to the combustion of pulverized fuel where the rate of temperature rise of fuel particles has been estimated at  $10^4$  °C/sec or more.<sup>2/</sup> Emphasis has therefore shifted to conditions of rapid heating.

In this study electrical pulse heating was employed to simulate the temperature transients experienced by fuel particles. The method combines the advantage of rapid heating with that of controlled energy input to the sample and a high probability for thermal equilibrium between sample and heat source. A constant heating rate of nearly  $10^4$  °C/sec was developed. The pulse heating technique has been used elsewhere<sup>3-4/</sup> for measurement of physical properties of conducting materials at high temperatures. Results are presented here on the devolatilization of a series of vitrains of different rank.

## EXPERIMENTAL

The procedure involved in these measurements consisted essentially of heating microgram quantities of coal by pulses of electrical current. The coal was contained in a cylinder of metallic screen which served as a resistance-heating element and at the same time retained the residue left after reaction. The yield of volatile products was determined from the weight loss of the coal sample after rapid heating.

Cylindrical screens, fabricated from 400-mesh, type 304, stainless steel wire cloth, were 6 cm long, 1.2 mm in diameter, and weighed 75 mg on average. When the screens were initially heated in vacuo, a significant weight loss occurred. Successive firings, however, produced no further weight changes. To eliminate this potential source of error, all screens were pre-fired at 900° C before determining their weights with a micro-balance.

Coal, having a particle size of 44-53  $\mu$ m, was introduced into the cylindrical screens, and the quantity of coal was determined by reweighing the screens. Typically, the amount of coal approximated 250  $\mu$ g. In some experiments, however, the coal charge was as small as 100  $\mu$ g or as large as 370  $\mu$ g. A correlation between quantity of coal sample and weight loss was sought, but none was found, and this result indicates that all of the coal samples reached thermal equilibrium with the heat source.

A cylindrical screen, containing coal, was clamped between electrodes, and the assembly was inserted into the vacuum system as shown in Figure 1. The pressure was reduced to 10-3 torr, and the system was then isolated from the pump. The screen was heated by an electrical current which was controlled to provide a constant time rate of increase of temperature. The circuit which controlled the current was designed to allow the current to increase as a function of time to compensate for the increase in resistance of the screen and the increase in radiant heat loss. In this mode of heating the increase in temperature of the screen was proportional to the length of time the current was applied.

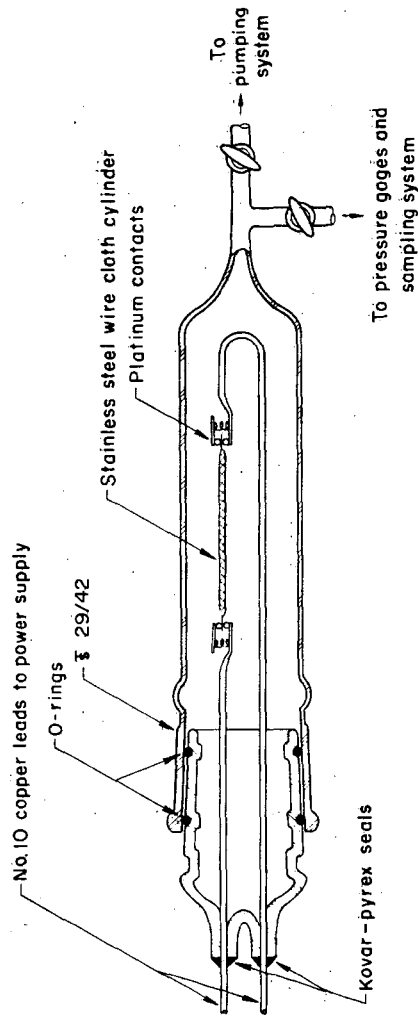


Figure 1 - Thermal decomposition assembly

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After firing, the screen with its residue from the reaction was removed from the system and reweighed. The resultant weight loss is a measure of the total volatile yield of gases and condensable products. The attendant pressure increase in the calibrated volume of the system is a measure of the gases evolved.

Calibration of screen temperature was accomplished by firing pure metals, comparable in weight and particle size to the coal samples, and observing the time required for them to melt. The condition of melting was determined by microscopic examination of the metal particles after heating. By this method the time to reach the melting point could not be pinpointed, but a time spread could be established for the extremes of complete melting and non-melting. The time spreads, indicated in Figure 2 for the different metals, amount to an uncertainty in temperature of at most  $\pm 70^\circ\text{C}$ . A line drawn through the mid-points of these time intervals corresponded to a constant heating rate of  $8.25 \times 10^3^\circ\text{C/sec}$ .

Proximate and ultimate analyses of the vitrains used in this study are presented in Table 1. The vitrains represent a wide range of volatile matter content, i.e., from 20.4 to 48.0 percent. The ash content has been kept low by careful selection of vitrain from the coal.

Table 1.--Analyses of vitrains

	Pocahontas No. 3 lvb	Pittsburgh hvAb	Illinois No. 2 hvcB
Proximate analysis (mf)			
Volatile matter	20.4	35.1	48.0
Fixed carbon	79.3	63.1	51.1
Ash	0.3	1.8	0.9
Ultimate analysis (maf)			
H	4.6	5.4	5.8
C	90.8	84.0	79.2
O	3.3	8.2	11.2
N	0.7	1.7	1.3
S	0.6	0.7	2.5

#### RESULTS AND DISCUSSION

Results of the decomposition of bituminous coals in the temperature region  $400\text{--}1160^\circ\text{C}$  are presented in Table 2 and graphed in Figure 3. The volatile yield or weight loss is the cumulative effect of reaction over an interval of rapidly changing temperature, and the temperatures designated in the table represent the maximum temperatures attained by the coal samples. The weight losses are averages of ten or more tests conducted at each temperature. Standard deviations indicated for the data points are larger than those generally obtained from physicochemical measurements on chemically pure materials. Lack of high precision was due to a number of factors: inhomogeneities in the coal itself; non-uniformities in the heating of the screens; and variability in the distribution of coal along the length of the cylinders.

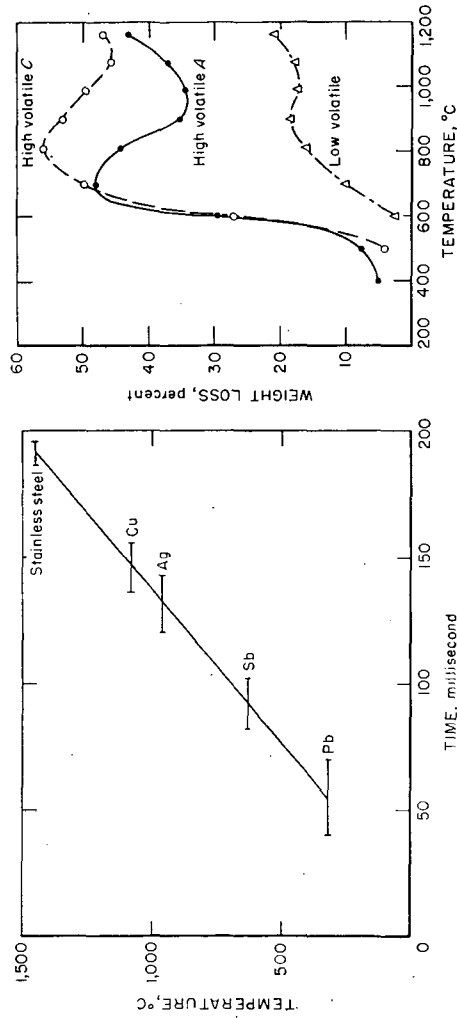


Figure 2 - Heating rate obtained by electrical pulse heating.

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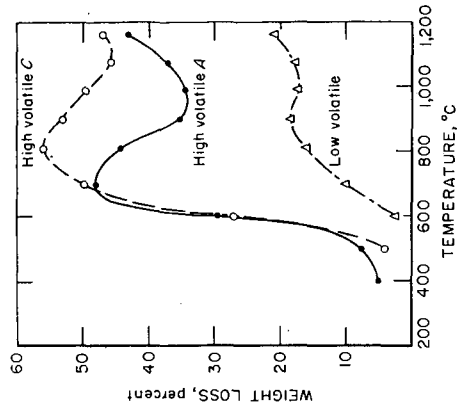


Figure 3 - Decomposition of vitrains from bituminous coals by rapid heating.

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Table 2.--Volatile yields from the decomposition of vitrains.

Temperature, °C	Weight loss, percent		
	Pocahontas No. 3, lvb	Pittsburgh, hvAb	Illinois No. 2, hvCb
400	--	4.9	--
500	0.0	7.6	4.1
600	2.4	29.4 ± 12	26.9 ± 8.2
700	10.0 ± 5.3	47.9 ± 3.2	49.7 ± 3.6
810	16.0 ± 2.3	44.1 ± 4.4	55.8 ± 1.6
900	18.5 ± 2.5	35.2 ± 4.8	53.0 ± 2.9
990	17.2 ± 1.4	34.5 ± 3.3	49.5 ± 3.4
1075	17.7 ± 2.1	37.1 ± 2.7	45.6 ± 2.5
1160	20.8 ± 1.9	43.1 ± 4.0	47.0 ± 1.9

The decomposition curves of Figure 3 obtained by heating vitrains at a rate of  $8.25 \times 10^3$  °C/sec, indicate that the release of volatiles is indeed rapid. Decomposition of hvC and hvA vitrains begins around 400° C as has been reported for slow heating studies of coal.<sup>5-6</sup> After the onset of reaction, volatile yields from the low rank coals quickly increase to a maximum in the region 700°-800° C. The maximum volatile yields are larger than the volatile matter of the coals determined by the standard ASTM method (Table 1), and in this respect our results are similar to those from other types of rapid heating studies.<sup>7-9</sup> With increase in temperature above 800°, there is a decrease in volatile yield to about the values given by proximate analysis. At 1160° C, which is the highest temperature attainable in this study, there is indication that the volatile yields from all coals are again trending upward.

The behavior of low volatile vitrain differs in some respects from that of the lower rank coals. Its threshold of reaction occurs at an elevated temperature of 600°. Its weight loss curve, although giving the appearance of a very weak peak at 900°, should most probably be construed as having reached a plateau in this region because the precision indices are too large to justify the existence of a real maximum.

The appearance of peaks in the weight loss curves from rapid heating is in marked contrast to the monotonic increase in weight loss that is observed when coal is devolatilized at a slow, constant heating rate.<sup>10</sup> A suggested explanation for the maxima in the weight loss curves of the low rank vitrains is that there is a competition between the bond-breaking reactions, which give rise to the initial decomposition products, and the recombination reactions, which cause initial products to form molecules more stable than the parent coal. Recently the idea of complex depolymerization and repolymerization reactions has been invoked to explain the ESR spectra of tars produced by the rapid pyrolysis of coal.<sup>11</sup>

Gases evolved during decomposition were measured by the pressure increase in the system. The moles of gas were converted to a weight basis by means of gas compositions reported in the literature,<sup>12</sup> and the amount of liquid or condensables was obtained by difference.

Table 3.--Dependence of gas-liquid composition of volatiles upon rank of vitrain.

Coal rank	Temperature °C	Coal weight μg	Total volatile yield		Gas yield		Liquid yield	
			μg	% of coal	μg	% of coal	μg	By diff. % of volatiles
Pocahontas No. 3 lvb	990	332	54	16	41	12	76	24
	900	282	46	16	33	12	72	28
Pittsburgh, hvAb	810	258	113	44	30	12	26	74
Illinois No. 2., hvCb	810	217	122	56	29	13	24	76

Gas and liquid yields corresponding to the maximum volatile yields from the coals are shown in Table 3. The gas yield in terms of  $\mu\text{g gas}/\mu\text{g coal}$  remains constant at about 12 percent, irrespective of the rank of the coal. At the same time the total yield of volatiles increased from 16 to 56 percent with decrease in coal rank. It is quite apparent, therefore, that the increased volatile yields obtained from the lower rank coals are due entirely to the increased formation of condensable products.

#### SUMMARY

Rapid pyrolysis of vitrains from bituminous coals was effected by heating them at a rate of  $8.25 \times 10^3$   $^{\circ}\text{C}/\text{sec}$ , and the extent of devolatilization was measured gravimetrically.

Yields of total volatiles from the low rank hvC and hvA coals do not increase monotonically with temperature, but instead reach a maximum in the temperature region  $700^{\circ}\text{--}800^{\circ}\text{C}$ . The peak volatile yields exceed the volatile matter contents of the coals that are determined by the standard ASTM method.

At temperatures above  $1100^{\circ}\text{C}$  there is evidence that the production of volatiles from all bituminous coals again increases with the temperature.

Low rank coals produce larger volatile yields than high rank coals. The increased yields are due almost entirely to increases in amounts of condensable reaction products.

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